EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.2: Fischer-Tropsch Mathematical Model and Reactor Scale-up Confirmation

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Disclaimer

Abstract

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using petroleum coke and ChevronTexaco's proprietary gasification technology. The objective of Phase I was to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation. The partners in this project are Texaco Energy Systems LLC. (a subsidiary of ChevronTexaco), General Electric (GE), Praxair, and Kellogg Brown & Root (KBR) in addition to the U.S. Department of Energy (DOE). ChevronTexaco is providing gasification technology and Fischer-Tropsch technology developed by Rentech, GE is providing combustion turbine technology, Praxair is providing air separation technology and KBR is providing engineering.

Each of the EECP subsystems were assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified F-T reactor scale-up as a potential technical risk. The objective of Task 2.3 was to confirm engineering models that allow scale-up to commercial slurry phase bubble column (SPBC) reactors operating in the churn-turbulent flow regime. In developmental work outside the scope of this project, historical data, literature references, and a scale-up from a 1 ½-in. (3.8 cm) to 6-ft (1.8 m) SPBC reactor have been reviewed. This review formed the background for developing scale-up models for a SPBC reactor operating in the churn-turbulent flow regime. The necessary fundamental physical parameters have been measured and incorporated into the mathematical catalyst/kinetic model developed from the SPBC and CSTR work outside the scope of this EECP project.

The mathematical catalyst/kinetic model was used to compare to experimental data obtained at Rentech during the EECP Fischer-Tropsch Confirmation Run (Task 2.1; reported separately). The prediction of carbon monoxide (CO) conversion as a function of days on stream compares quite closely to the experimental data.

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The Contractor cannot confirm the authenticity of the information contained herein since this report is being submitted under the U.S. Department of Energy requirement that the electronic files must be submitted without being write-protected.

Note: Unless specified otherwise, all quarters/years are calendar quarters/years.

Executive Summary

This report summarizes Task 2.2: Mathematical Modeling of Phase II of the development of the Early Entrance Coproduction Plant (EECP) being performed under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FC26-99FT40658. The EECP will integrate advanced high efficiency, fuel flexible electrical power generation (gasification) with a facility capable of producing clean transportation fuels and/or chemicals. An industrial consortium consisting of Texaco Energy Systems LLC (TES), Kellogg Brown & Root (KBR), General Electric (GE), Praxair, and Rentech is developing this project.

The overall objective of this project is the three phase development of an EECP which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

The EECP converts petroleum coke into synthesis gas in the Gasification section. Approximately 1,120 metric tons (1,235 short tons per day) petroleum coke is used to produce 55 megawatts of net electric power for export, approximately 617 barrels per day of Fischer-Tropsch (F-T) products (finished high-melt wax, finished low-melt wax, F-T diesel, and F-T naphtha), steam, and approximately 81 metric tons (89 short tons per day) of sulfur. Additionally, the Air Separation Unit (ASU) will produce nitrogen and oxygen for export.

Each of the EECP subsystems was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified F-T reactor scale-up as a potential technical risk. The objective of Task 2.3 was to confirm engineering models that allow scale-up to commercial slurry phase bubble column (SPBC) reactors operating in the churn-turbulent flow regime. In developmental work outside the scope of this project, historical data, literature references, and a scale-up from a 1 ½-in. (3.8 cm) to 6-ft (1.8 m) SPBC reactor have been reviewed. This review formed the background for developing scale-up models for a SPBC reactor operating in the churn-turbulent flow regime. The necessary fundamental physical parameters have been measured and incorporated into the mathematical catalyst/kinetic model developed from the SPBC and CSTR work outside the scope of this EECP project. The mathematical model was successfully used by TES outside of the EECP Project during the F-T demonstration at the LaPorte Alternative Fuels Development Unit (AFDU).

Background

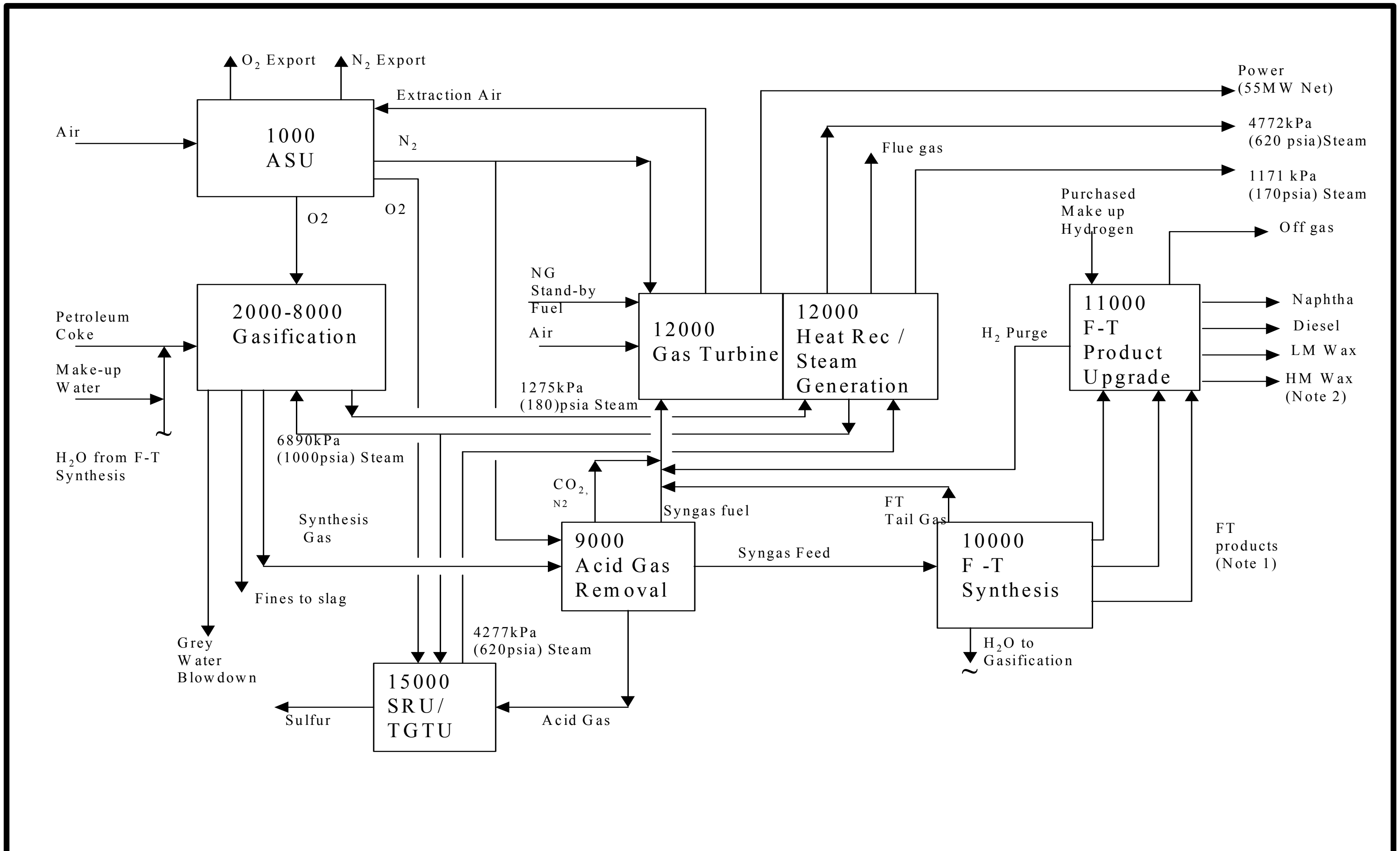
The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, Fischer-Tropsch (F-T) diesel, F-T naphtha, elemental sulfur, and will consume approximately 1,235 short tons per day of petroleum coke. The EECP Concept is illustrated in Schematic 1.

Petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit. This coke slurry is mixed with high-pressure oxygen from the Air Separation Unit (ASU) and a small quantity of high-pressure steam in a specially designed feed injector mounted on the gasifier. The resulting reactions take place very rapidly to produce synthesis gas, also known as syngas, which is composed primarily of hydrogen, carbon monoxide, water vapor, and carbon dioxide (CO_2) with small amounts of hydrogen sulfide, methane, argon, nitrogen, and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. Approximately 75% of the synthesis gas is treated in the AGR to remove the bulk of H_2S with minimal CO_2 removal and then forwarded as fuel to the GE frame 6FA gas turbine. The remaining 25% of the stream is treated in the AGR to remove CO_2 and H_2S and then passed through a zinc oxide bed arrangement to remove the remaining traces of sulfur before being forwarded to the F-T Synthesis Unit. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release CO_2. The resulting CO_2 and nitrogen mixture is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides emissions. The bulk of the nitrogen from the air separation unit is sent to the gas turbine as a separate stream and combined in the combustion chamber with the syngas fuel to increase the power production and reduce nitrogen oxide emissions from the gas turbine.

In the F-T reactor, carbon monoxide and hydrogen react, aided by an iron-based catalyst, to form mainly heavy, straight-chain hydrocarbons. Since the reactions are highly exothermic, cooling coils are placed inside the reactor to remove the heat released by the reactions. Three hydrocarbon product streams, heavy F-T liquid, medium F-T liquid and light F-T liquid are sent to the F-T product upgrading unit while F-T water, a reaction byproduct, is returned to the Gasification Unit. The F-T tail gas and AGR off gas are fed to the gas turbine and mixed with syngas. This increases electrical power production by 11%.

In the F-T Product Upgrading Unit (F-TPU), the three F-T liquids are combined and processed as a single feed. In the presence of a hydrotreating catalyst, hydrogen reacts slightly exothermally with the feed to produce saturated hydrocarbons, water, and some hydrocracked light ends. The resulting four liquid product streams are naphtha, diesel, low-melt wax, and high-melt wax that leave the EECP facility via tank truck.

The power block consists of a GE PG6101 (6FA) 60 Hertz (Hz) heavy-duty gas turbine generator and is integrated with a two-pressure level heat recovery steam generator (HRSG) and a non-condensing steam turbine generator. The system is designed to supply a portion of the compressed air feed to the ASU, process steam to the refinery, and electrical power for export and use within the EECP facility. The gas turbine has a dual fuel supply system with natural gas



Kellogg Brown & Root, Inc. A Halliburton Company Engineering services by Halliburton Technical Services, Inc.	NOTES: 1. Includes Light, Medium and Heavy FT Liquid product streams 2. LM = Low Melt HM = High Melt

DOE EARLY ENTRANCE COPRODUCTION PLANT
PORT ARTHUR REFINERY

OVERALL BLOCK FLOW DIAGRAM

DRAWN JSA	DATE 10/10/0	DOE AWARD NUMBER: DE-FC-99FT40658	REV.
DESIGNER	DATE	SUBCONTRACTOR PROJECT NO: 9202	0
CHECKED	DATE	TASK NO: 4.1.2	
APPROVED	DATE	DRAWING NO: KBR-P-BFD-0001	

Schematic 1 – EECP Concept

as start-up and backup fuel, and a mixture of syngas from the gasifier, offgas from the AGR Unit, and tail gas from the F-T Synthesis Unit as the primary fuel. Nitrogen gas for injection is supplied by the ASU for nitrogen oxides (NOx) abatement, power augmentation, and the fuel purge system.

The Praxair ASU is designed as a single train elevated pressure unit. Its primary duty is to provide oxygen to the gasifier and Sulfur Recovery Unit (SRU), and to satisfy all of the EECP's requirements for nitrogen, instrument air, and compressed air. Nitrogen produced by the ASU is used within the EECP as a stripping agent in the AGR Unit, as diluents in the gas turbine where its mass flow helps increase power production and reduce NOx emissions, and as an inert gas for purging. The gas turbine, in return for diluent nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor and oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums and then to the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS off gas, oxygen, and air to a burner. In the thermal reactor, the hydrogen sulfide (H_2S), a portion of which has been combusted to sulfur dioxide (SO_2), starts to recombine with the SO_2 to form elemental sulfur. The reaction mixture then passes through a boiler to remove heat while generating steam. The sulfur-laden gas is sent to the first pass of the primary sulfur condenser where all sulfur is condensed. The gas is next preheated before entering the first catalytic bed in which more H2S and SO_2 are converted to sulfur. The sulfur is removed in the second pass of the primary sulfur condenser, and the gas goes through a reheat, catalytic reaction, and condensing stage two more times before leaving the SRU as a tail gas. The molten sulfur from all four condensing stages is sent to the sulfur pit, from which sulfur product is transported off site by tank truck.

The tail gas from the SRU is preheated and reacted with hydrogen in a catalytic reactor to convert unreacted SO_2 back to H2S. The reactor effluent is cooled while generating steam before entering a quench tower for further cooling. A slip stream of the quench tower bottoms is filtered and sent along with the condensate from the SRU knockout drums to the SWS. H_2S is removed from the quenched tail gas in an absorber by using lean methyldiethanolamine (MDEA) solvent from the AGR Unit. The tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

During Phase I, each of the EECP subsystems was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified the scale-up of the F-T reactor as a potential high technical and high economic risk to the EECP. The overall risk to the EECP was ranked as medium due to the fact that the proposed EECP is designed to produce power as the primary product.

The objective of Task 2.3 was to confirm engineering models that allow scale-up to commercial slurry phase bubble column (SPBC) reactors operating in the churn-turbulent flow regime. In developmental work outside the scope of this project, historical data, literature references, and a scale-up from a 1 ½-in. (3.8 cm) to 6-ft (1.8 m) SPBC reactor have been reviewed. This review formed the background for developing scale-up models for a SPBC reactor operating in the churn-turbulent flow regime. The necessary fundamental physical parameters have been measured and incorporated into the mathematical catalyst/kinetic model developed from the SPBC and CSTR work outside the scope of this EECP project.

Results and Discussion

The ChevronTexaco proprietary mathematical model is a simple multi-component numerical model including detailed kinetics and was constructed to predict reactor performance for F-T synthesis in a bubble column slurry reactor. The model assumes that the gas phase travels in plug flow, the liquid phase is completely back-mixed, the mass transfer resistance is in the liquid phase, the catalyst is evenly distributed throughout the column, intraparticle resistances are negligible, hydrodynamic and physicochemical properties are spatially independent, and the reactor operates in an isothermal, isobaric and steady-state regime. The gas phase balance equation for each component is solved using a fourth order Runge-Kutta method, and a secant method is used as an iterative procedure to obtain closure for the liquid phase concentrations.

The ChevronTexaco proprietary mathematical model was used to predict Rentech's bubble column reactor (BCR) performance for Task 2.1.3: F-T Confirmation Run (RI74). Rentech's BCR is 1.5 inches internal diameter (id) x 26 feet (38 millimeter id x 8 meters) tall. The mathematical model was successfully used by TES outside of the EECP Project during the F-T demonstration at the LaPorte AFDU.

In Phase I of the EECP project certain assumptions were made relative to operation and performance of the F-T subsystem. These assumptions were necessary in order to allow economic assessments to be made. The BCR test was conducted to confirm those assumptions. The synthesis gas hydrogen (H_2) to carbon monoxide (CO) ratio used in the test was equivalent to the expected EECP H_2 to CO ratio (under 0.8). Rentech's proprietary catalyst activation procedure was used to prepare the catalyst. The test was conducted at the ChevronTexaco/Rentech proprietary temperature, pressure, and space velocity. Carbon dioxide (CO_2) was added during the test to determine its effects on the F-T catalyst.

The kinetic expressions used by the model were identical to the ones used in a previous F-T run (RI66) at Rentech. Figure 1 shows the comparison between the predicted results (Model) and the experimental (Expt.) data for CO conversion as a function of days on stream (DOS). During the F-T Confirmation Run, catalyst was added to the reactor to increase slurry concentration to the EECP design basis point. The model compares quite closely to the magnitude of the conversions and is able to account for increases in catalyst concentration and average reactor temperature (day 11). However, the model is unable to predict the response of conversion after each addition is made – the slopes of the lines are much less than the experimental data. This difference could be attributed to the large uncertainty in calculating the amount of catalyst within the reactor for any given period of time.

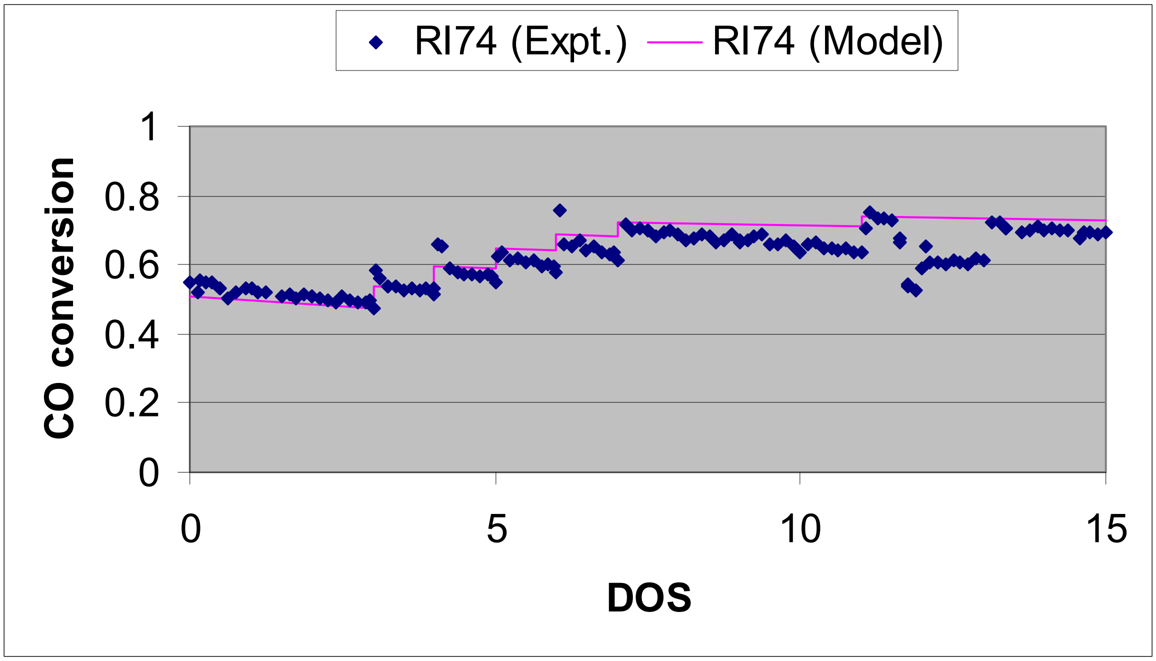


Figure 1: CO conversion as a function of days on stream (DOS).

Conclusions

The scale-up of the F-T BCR from the 1.5-inch (38 millimeter) id bench-scale reactor to an 8-foot (2.4 meter) id or larger demonstration-scale reactor presents a major technical challenge. ChevronTexaco's proprietary mathematical model will be used in the design of the EECP F-T reactor. The model developed outside of the EECP Project compares closely to experimental data acquired from Rentech's BCR. The model was also successfully used outside of the EECP Project in the F-T demonstration at the LaPorte AFDU (22 inch/0.56 meter id reactor). Based on the testing results, the team feels the risk in the EECP F-T reactor scale-up has been reduced.

List of Acronyms and Abbreviations

AFDU	Alternate Fuels Development Unit
AGR	Acid Gas Removal
ASU	Air Separation Unit
BCR	Bubble Column Reactor
Btu	British thermal unit
CO_2	Carbon Dioxide
CO	Carbon Monoxide
DOE	Department of Energy
DOS	days on stream
EECP	Early Entrance Coproduction Plant
Expt.	Experimental
F-T	Fischer-Tropsch
F-TPU	Fischer-Tropsch Product Upgrading
GE	General Electric
Hz	Hertz
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulfide
HRSG	Heat recovery steam generator
id	Internal Diameter
KBR	Kellogg Brown & Root
kPa	Kilopascal
MDEA	Methyldiethanolamine
MW	Megawatt
N_2	Nitrogen
NOx	Nitrous oxide
O_2	Oxygen
Psia	Pounds per square inch - atmosphere
RD&T	Research, Development, and Testing
SO_2	Sulfur Dioxide
SPBC	Slurry Phase Bubble Column
SRU	Sulfur Recovery Unit
SWS	Sour Water Stripper
TES	Texaco Energy Systems LLC